

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of Filled Polyamides

We, ICI FIBRES LIMITED, of Pontypool, Monmouthshire, Great Britain, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to high molecular weight synthetic linear polyamides containing inert fillers in the form of mineral hydrated aluminium silicates, which are particularly, although not exclusively, to be used in the melt spinning of filaments.

These aluminium silicates correspond approximately to the formula $\times \text{Al}_2 \text{O}_3 \cdot y \text{Si}$

$\text{O}_2 \cdot z \text{H}_2\text{O}$, although up to 2% of other compounds, such as the oxides of iron, titanium, calcium, magnesium, potassium and/or sodium may be present as impurities, or chemically combined therewith.

Synthetic linear polyamides, e.g., polyhexamethylene adipamide are widely used for making textile and other products, for instance filaments, fabrics, which are noted for their attractive properties e.g., tenacity, which are superior to those of natural fibres and rayons. The polyamides are, however, somewhat more expensive to manufacture than the latter.

Examples of synthetic linear polyamides and their starting compounds are:—

Starting compounds	Linear polyamides
epsilon-caprolactam	poly-epsilon-caprolactam
omega-aminoundecanoic acid	poly-omega-aminodecanoic acid
hexamethylene diammonium adipate	polyhexamethylene adipamide
hexamethylene diammonium sebacate	polyhexamethylene sebacamide
octamethylene diammonium adipate	polyoctamethylene adipamide
decamethylene diammonium sebacate	polydecamethylene sebacamide

A cheap filler should be capable of being mixed with the polyamide without interfering with the capability of the polyamide of being melt-spun into filaments, despite the minuteness of the spinneret orifices often employed and the filters through which the polyamide is normally passed before it enters the spinneret. Thus the use of many fillers which would offer advantages in cost alone, are unacceptable from these points.

Hydrated aluminium silicates of mineral origin possess this property.

According to the invention of British patent specification No. 1,020036, a high molecular weight synthetic linear polyamide composition having in admixture a filler selected from the group consisting of the mineral hydrated aluminium silicates Kaolin and Fuller's earth, the mixture having between 20 and 40% by weight of the mineral hydrated aluminium

silicate.

These aluminium silicates correspond approximately to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$.

5 When materials are to be incorporated in polyamides, it is advantageous, if not essential, to add the materials to the polyamide-yielding compounds used in the manufacture of the polyamides before the polymerisation takes place by known techniques. Hydrated aluminium silicates may be added to the polyamide-yielding compounds because they do not appreciably interfere with the course of the manufacture, remaining chemically inert during the polymerisation process. It will be understood, however, that the hydrated aluminium silicates may be added at any stage during the manufacture of the polyamide or they can be incorporated in the finished polyamide.

20 According to another aspect of the above-mentioned prior patent specification in a process for the manufacture of a polyamide composition containing a mineral hydrated aluminium silicate selected from Kaolin and Fuller's earth, the polymerisation of the polyamide-yielding compounds taking place in admixture with the mineral hydrated aluminium silicate, the mixture having between 20 and 40% by weight of mineral hydrated aluminium silicate.

35 Alternatively, the aluminium silicate may be mixed with and dispersed in an aqueous solution of 5% by weight of the polyamide having a numerical average degree of polymerisation of 1-12. The aluminium silicate is thoroughly mixed with, and dispersed in, the latter, conveniently by milling therewith, so that a dispersion is formed. The dispersion is then mixed with the remainder of the polyamide-yielding materials and the polymerisation completed.

45 The filler may be added before the polymerisation of the polyamide-yielding compounds has taken place, or at any stage in the polymerisation process.

50 Further, the filler may be added to the major portion of the polyamide, either before the polymerisation of this portion is initiated, or completed, in the form of a slurry, together with a minor portion of the polyamide, which is partially polymerised. The polymerisation is completed when the two portions and the filler are mixed together.

55 The inclusion of 20% Kaolin does not increase the abrasiveness to the pumps, guides and other components used in the spinning of the filaments as compared to the inclusion of 20% of some other form of filler. Thus the mixture offers advantages over the use of other diluted polyamide mixtures and, in particular, renders a spinning process far more reliable, by reducing the number of pump failures and filaments breaks in the spinning operation, (or by reducing filament

breaks in a subsequent drawing or twisting process.

The refractive index of Kaolin is substantially identical to that of the polyamide and consequently a mixture containing Kaolin has the same appearance as the polyamide.

70 The tenacity of the filaments produced from an 80:20 nylon 6.6-Kaolin mixture is surprisingly high, although, of course, lower than the value of the undiluted yarn. The filaments produced from the mixture is adequate for most end uses, where the exceptionally high tenacity of undiluted polyamide is greater than is normally required, for example, filaments for use in carpets.

80 Different maximum particles sizes of Kaolin were tried, and the various mixtures produced had only slightly different properties. The finer grade filler gave a yarn with a higher tenacity, and the filtering pack used in the spinning process had a longer life.

85 Although a small addition of the Kaolin lowers the tenacity of the filaments somewhat, as the proportion of Kaolin present increases, the tenacity still remains at an acceptably high value. Consequently, the proportion of filler preferred is in the range 20 to 40% by weight of the polyamide so that a worthwhile saving in cost is made.

95 If the proportion of the filler is more than 50% by weight of the polyamide the viscosity of the melt increase to an extent whereby it is difficult to extrude the mixture.

100 It is an object of the present invention to dilute polyamides with relatively cheap fillers and yet retain in the polyamides commercially useful properties, in particular, that there should be no diminution in the tenacity of the filaments produced from the diluted polymer. There are many end uses for which as high a tenacity as possible is desirable.

105 Thus it is an object of the present invention to provide a filled polyamide composition, filaments spun from which has a value for the tenacity substantially higher than that for the diluted filaments according to above-mentioned prior patent specification.

110 It has been found that the relative weakness in the strength of the filled filaments is due to aggregates of the filler occurring in the filament structure, whereas, if the filler could be uniformly dispersed relative weak spots in the filaments would be eliminated.

120 It is known to cause the uniform dispersion of pigments in the polyamide prior to extrusion by causing initially the coating of the pigments with partially polymerised polyamide composition, the polyamide comprising the coating composition, perhaps, differing from the polyamide comprising the major part of the mixture. In this case, the coating composition was present in the mixture in an amount which was a substantial portion, say, 20% of the amount of the polyamide forming

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the major part of the mixture.

According to the present invention a composition of a high molecular weight synthetic linear polyamide in admixture with a filler of a mineral hydrated aluminium silicate in particulate form, has the constituent particles of the filler previously coated with a lactam, or amino acid, or a partially polymerised product thereof before the addition to the polyamide forming the major part of the mixture.

An example of a synthetic linear polyamide which may form the major part of the mixture is poly(hexamethylene adipate) (nylon 66), and the coating material may be, for example:—

epsilon-caprolactam or poly(epsilon-caprolactam) (nylon 6),
epsilon-enantholactam or poly(epsilon-enantholactam) (nylon 7),
omega-aminoundecanoic acid or poly(omega-amino undecanoic acid) (nylon 11).

Conveniently, the coating material is present in an amount comprising less than 5% by weight of the amount of the polyamide forming the major part of the mixture.

It is convenient to coat the filler with a lactam or amino acid, or to polymerise the coating material to an extent whereby the coated filler remains workable in an autoclave i.e. the material does not set in a solid form in the autoclave. It will be appreciated that completely polymerised coating material may be employed if the polymerisation is effected by a solid state polymerisation process, but the use of such a process offers no advantage with respect to the present invention.

In such a mixture it is found that the properties are not substantially affected by the presence of the coating material, whereas, otherwise, a composition having different properties would result, i.e. these properties corresponding approximately to the summation of the properties of the constituents of the mixture.

It is found that, by pre-coating the filler, it does not form aggregates in the resulting mixture, and it is believed that this better dispersion of a coated filler particles, compared to untreated mineral hydrated aluminium silicates, is due to the elimination of surface ions from the particles.

Adhesion between the aluminium silicate particles and, say, nylon 6, and between the nylon 6 and the polyamide to be filled, is not believed to be the cause of the better dispersion characteristics. Upon drawing a filament, produced from a mixture according to the present invention, lacunae do form, although possibly they are reduced in extent compared to the case where the filler particles are not coated.

The forms of mineral hydrated aluminium silicate which are particularly advantageous

for use according to the invention referred to in the prior patent specification mentioned above, and for use according to the present invention are:—

Kaolin (or Kaolinite), and
Fuller's Earth.

The particle sizes of the aluminium silicate may be between 0.1—10 microns, for preferably between 0.1 and 2 microns, for example, when the composition is to be melt-spun into filaments for textile use.

According to another aspect, the present invention resides in a process for the production of a composition comprising a high molecular weight synthetic linear polyamide and a filler comprising mixing a mineral hydrated aluminium silicate in particulate form the particles of which are coated with a solid lactam or solid amino monocarboxylic acid or a partly polymerised product thereof with unpolymerised or partly polymerised materials used for forming said synthetic linear polyamide and thereafter polymerising both polyamide-forming components of the mixture so made to form the said composition.

The coated filler may be added to polyamide-yielding compounds, which are used to form the polyamide comprising the major part of the mixture, the polymerisation of the polyamide-yielding compounds being arranged to take place, or to be completed, in admixture with the pre-treated mineral hydrated aluminium silicate.

Thus, the treated aluminium silicate may be added before the polymerisation of the polyamide comprising the major part of the mixture has taken place, or at any stage in the polymerisation process, or it can be incorporated in this polyamide when completely polymerised.

The polymerisation of the coating material, however, is arranged to take place, or to be completed in admixture with the polyamide, or partially-polymerised, or polyamide-yielding compounds, comprising the major part of the mixture.

The invention also includes the shaping of the resulting polyamide/aluminium silicate mixture, for instance, the melt-extrusion thereof into filaments, films and other elongated articles, and articles made thereby.

Three examples according to the present invention will now be described, but not by way of limitation of the scope of the invention.

EXAMPLE 1

800 parts of Kaolin in powdered form are dispersed in 2550 parts of water by rapid stirring. 80 parts of caprolactam are dissolved in this slurry and this is stirred in an autoclave containing an atmosphere of nitrogen. The temperature is raised to 210°C and the pressure to 250 pounds per square inch over a period of 2 hours and these conditions are maintained for a further 1½ hours, before

the pressure is reduced to atmospheric pressure during another 1 hour. The resultant mixture is cooled in a nitrogen atmosphere and is broken up into a finely divided form and dried.

- 5 10 parts of this mixture, which comprises Koalin particles coated with nylon 6, is intimately mixed with 40 parts of partially polymerised nylon 66 (prepared by heating
10 58 parts of hexamethylene diammonium adipate and 0.067 parts of acetic acid together in a nitrogen filled sealed glass tube at 220°C for 3 hours). This mixture is heated under an atmosphere of steam at 285°C for 1½ hours,
15 stirring being carried out during this period.

The filled polymer made as above was melt spun into yarn. The yarn had five filaments and was drawn in the solid state over a large diameter hot pin at 120°C to five times its original length and had a final denier of 30.

The values of certain properties of the yarns produced from the nylon 66-filler mixture prepared according to this example are compared with the values obtained for yarns obtained from a filled mixture prepared according to the present applicants' above-mentioned prior patent specification and with undiluted nylon 6.6, when drawn to five times their original length, in the following table

TABLE

	80:20 Nylon 66/ Coated Kaolin	100% Nylon 66	80:20 Nylon 66/ Uncoated Kaolin
Draw Ratio	5.0	5.0	5.0
Tenacity (Grams/denier)	5.2	6.2	3.7
Extensibility (%)	17	22	17

- (The results given in the corresponding Table in the prior patent specification were obtained for yarn which had been melted under steam at atmospheric pressure, while the three yarns considered in the Table above had been
35 rod spun).

EXAMPLE 2

- 10 parts of coated Kaolin particles, prepared by the method described in Example 1 are
40 intimately mixed with 46.4 parts of hexamethylene diammonium adipate and heated together with 0.053 parts of acetic acid in a nitrogen filled, sealed glass tube at 220°C for 3 hours. After cooling, the tube is opened
45 and the contents of the tube broken up, and heated under an atmosphere of steam at 285°C for 1½ hours, stirring being carried out during this period.

- The resulting mixture was melt spun into
50 yarn. This yarn had five filaments and was drawn in the solid state over a large diameter hot pin at 120°C to 5 times its original length. The resulting yarn had a final denier of 25 and a tenacity of 5.2 grams per denier and
55 an extensibility of 17%.

EXAMPLE 3

- 4 parts of caprolactam are dissolved in 30 parts of water and the solution added slowly with stirring to 40 parts of kaolin in a beaker,
60 to give a thick creamy paste. This is dried and

broken up into a finely divided form.

11 parts of this mixture which comprises kaolin particles coated with caprolactam, is intimately mixed with 46.4 parts of hexamethylene diammonium adipate and heated together with 0.053 parts of acetic acid in a nitrogen filled sealed glass tube for 3 hours at 220°C. After cooling, the tube is opened and the contents broken up and heated under an atmosphere of steam at 285°C for 1½ hours, stirring being carried out during this period.

The filled polymer prepared in this way was melt spun into a yarn which had 5 filaments, and was drawn in the solid state over a large diameter pin at 120°C to 5 times its original length. The resulting yarn had a final denier of 25 and a tenacity of 5.0 grams per denier and an extensibility of 25%.

The filaments drawn are opaque due to lacunae being formed adjacent to the Kaolin particles, and this also gives the yarn a chalky appearance when dyed. Fabrics made from such filaments are suitable for lining, blouses and shirts.

WHAT WE CLAIM IS —

1. A process for the production of a composition comprising a high molecular weight synthetic linear polyamide and a filler comprising mixing a mineral hydrated aluminium silicate in particulate form the particles of which are coated with a solid lactam or solid

- amino monocarboxylic acid of a partly polymerised product thereof with unpolymerised or partly polymerised materials used for forming said synthetic linear polyamide and thereafter polymerising both polyamide-forming components of the mixture so made to form the said composition
- 5 2. A process as claimed in claim 1 wherein the particle coating material comprises less than 5% by weight of the polyamide constituting the major part of the mixture.
- 10 3. A process as claimed in claim 1 in which the coating material comprises epsilon caprolactam.
- 15 4. A composition produced by the process claimed in claims 1, 2 or 3.
5. A composition as claimed in claim 4 wherein the major part of the polyamide is polyhexamethylene adipamide.
6. A composition as claimed in claim 4 comprising an amount of filler which is 20% to 40% by weight of the composition.
7. A composition as claimed in claim 4 wherein the mineral hydrated aluminium silicate is Fuller's Earth or Kaolin.
8. Shaped articles made from the composition as claimed in claim 4.
9. A composition as claimed in claim 4 and substantially as described herein with particular reference to examples 1, 2 and 3.
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